AVCO EVERETT

RESEARCH LABORATORY

a division of
AVCO CORPORATION

(U) STUDY OF THERMAL RADIATION ASSOCIATED WITH

NON-EQUILIBRIUM FLOW IN THE APOLLO

FLIGHT REGIME

Quarterly Progress Report

Contract NAS 9-136

June 15, 1962

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MANNED SPACECRAFT CENTER

APOLLO PROCUREMENT OFFICE

Houston 1, Texas

STUDY OF THERMAL RADIATION ASSOCIATED WITH NON-EQUILIBRIUM FLOW IN THE APOLLO FLIGHT REGIME
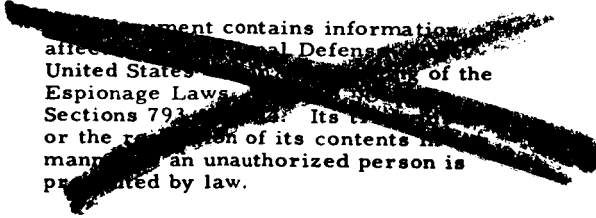
QUARTERLY PROGRESS REPORT

Contract NAS 9-156

June 15, 1962

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION MANNED SPACECRAFT CENTER APOLLO PROCUREMENT OFFICE
Houston 1, Texas

THIS PAGE IS BLANK

1. Electric Shock Tube Studies

Absolute measurements of the radiation from normal intensity shocks in air have been continued in the electric shock tube at velocities up to 36,200 ft/sec and at initial pressures ranging down to 0.1 mm Hg. Concentrated efforts have been made to measure the equilibrium and non-equilibrium radiation behind a normal air shock at 33,000 ft/sec at an initial pressure of 0.1 mm Hg. The integrated non-equilibrium radiation has been found to be approximately 36 watts/cm^2-2π ster as reported in the Phase I Report.[1] This radiation as well as the equilibrium radiation was found to be comprised mostly of N_2^+(1-) molecular band radiation, N-atom line radiation and Kramer's radiation.

Our understanding of air radiation has been derived primarily from studies of hot gas samples under equilibrium conditions. By the normalization of theory to measurements, quantities such as f numbers and effective nuclear charges have been obtained. Previously the highest temperatures under which these studies were made was approximately 8,000°K and this condition was obtained by reflected shock techniques.[2] The present study of normal shocks has enabled us not only to examine the non-equilibrium radiation at high velocities but has also enabled us to extend our study of high temperature equilibrium air into the 10,000°K range.

Figure 1 shows the equilibrium radiation measurements from normal air shocks at U_s = 33,000 ft/sec and p_1 = 0.1 mm Hg. Theoretical distributions of the N_2 (2+), N_2^+(1-) and Kramer's radiation (produced by the capture of electrons by nitrogen ions) are also plotted in this figure. The f numbers used for the N_2 (2+) and the N_2^+(1-) systems are those reported in Refs. 2 and 3 respectively. Other radiating molecular band systems should contribute insignificant amounts of radiation at this condition due to the high degree of dissociation. The dotted line is drawn for free-bound nitrogen Kramer's radiation from Kivel and Bailey.[4] This estimate did not account for the fine structure of this radiation at short wavelengths. The solid line is drawn from a calculation by Lindenmeier[5] which takes into account this fine structure. An effective nuclear charge, Z^2, of 1.4 was used in Lindenmeier's calculation. Comparison between this theory and the experiments from Fig. 1 indicates that this value should be reduced somewhat.

The locations of atomic nitrogen line radiation as reported in Ref. 2 are also plotted in this figure. These atomic lines quite clearly correspond to the main source of radiation between 0.5 and 1.0 microns wavelength. By assuming that the atomic lines are black body limited, one can estimate a maximum radiation intensity by using the doppler width of the lines.

This estimate under the conditions of the measurements in Fig. 1 amounts to approximately 12 watts/cm^3-2π ster. The total equilibrium
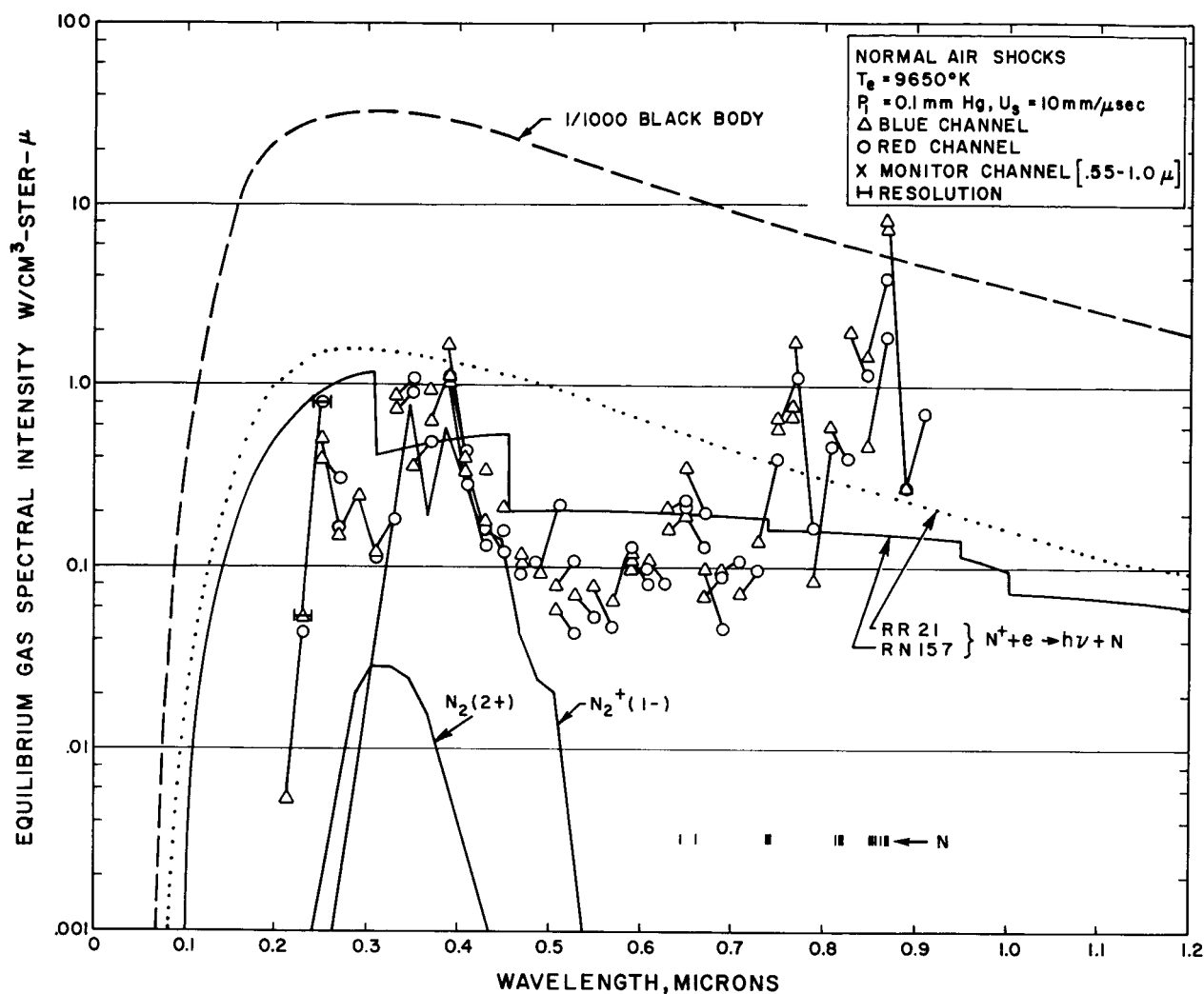
Fig. 1   Equilibrium radiation measurements behind normal air shocks
versus wavelength.   The shock conditions are U_s = 10 mm/μsec,
P_1 = 0. 1 mm Hg.   The equilibrium temperature is 9650°K.

radiation reported by Kivel and Bailey[4] under these conditions was only about 8 watts/cm^3-2π ster; this reference did not include any atomic line radiation. By integrating under the curve of the measurements in Fig. 1 about 3 watts/cm^3-2π ster can be attributed to the atomic line radiation and about 3 watts/cm^3-2π ster to the remainder. Only this latter value should be compared with the 8 watts/cm^3-2π ster estimated by Kivel and Bailey.[4] The discrepancy is attributed tentatively to an over-estimate of the Kramer's radiation.

Needless to say Kramer's radiation is very sensitive to electron concentration. A better measurement of Kramer's radiation should be made at higher degrees of ionization where estimates of electron and ion concentration are less subject to error. Other measurements should be made through a variety of gas sample thicknesses to test at what conditions atomic line radiation becomes black body limited.

In our non-equilibrium radiation measurements, atomic nitrogen line radiation has been found to be of the same relative intensity to the total radiation as has been found in the case of equilibrium radiation. However, the total non-equilibrium radiation intensity value of 36 watts/cm^2 2π ster, reported in the Phase I[1] report for a normal air shock at 33,000 ft/sec and p_1 = 0.1 mm Hg is still a reasonably good estimate. During the last three months, additional time to peak and time to 10% above equilibrium intensity values have also been obtained. These measurements were substantially the same as our previously reported results.

Recently, in conjunction with electronic heat transfer measurements, optical measurements were made of the gas cap radiation on the nose of spherical models. Analysis of this data is yet in a preliminary stage but qualitative analysis of the gas cap radiation shows significantly higher radiation intensity than that seen from the normal shock wave. These measurements will be invaluable in conjunction with heat transfer measurements to evaluate the steady test time and also to properly estimate radiation heat transfer effects simulated super-satellite re-entry velocities and altitudes. Further analysis of this important source of data is planned.

Experimental and theoretical studies are being conducted in gases other than air to lend insight into the physics and chemistry of the non-equilibrium region. The following sections outline these efforts at AERL.

2. Shock Front Radiation-Experimental Study of Collision Limiting*

An experimental program is in progress to determine the density at which various radiative band systems of shock heated air become collision limited.[2] Since the results are easier to interpret in a pure gas, data have

---

been collected on the N_2^+ first negative (3900-3925 A) and N_2 first positive (5000-10,000 A) band systems in nitrogen covering a range of initial pressures of 20-500μ Hg and shock velocities of 4.5 - 7.0 mm/μ sec.

Analysis of the radiation profiles in the shock front indicates that the binary scaling law begins to break down at the lower initial pressures. Before collision limiting sets in the kinetic processes responsible for the radiation overshoot involve only binary collisions. Therefore, the intensity of radiation overshoot is expected to be proportional to density while the duration of the overshoot is inversely proportional to density.[6] This binary scaling effect is shown in Fig. 2 for the N_2^+ first negative band in nitrogen. Two radiation profiles taken at the same shock velocity but at initial pressures of 100 and 200μ Hg have been plotted using the binary scaling law. The two profiles are observed to practically coincide. However, in Fig. 3 four other radiation profiles, two at 100μ and two at 20μ Hg plotted in a similar manner, are seen not to scale.

If this breakdown of binary scaling between 100 and 20μ Hg initial pressure is ascribed to collision limiting, and, if the assumption is made that all the atomic and molecular species in the gas are effective in deactivating the excited electronic state of the N_2^+ first negative system, then this data indicates that the collisional deactivation cross-section is greater than 3×10^{-14} cm^2.[2]

A thorough analysis of the parameters characterizing the radiation profile is currently being carried out to ascertain, if possible, whether the effect observed is indeed due to collision limiting of the excited electronic state. The range of initial pressure is being extended to higher values to check that the binary scaling law holds into a pressure range where collision limiting is definitely not expected to occur. This higher pressure data will also allow comparison with other data previously obtained in chemical and electric shock tubes.

3. An Investigation of the Luminous Front Excitation Mechanism in Shock-Heated N-N_2 Mixtures *

Much is known about the radiation emanating from shock-heated nitrogen.[2,3,7] The important band systems have been identified and the f numbers measured. The N_2 (1+) and N_2^+ (1-) radiation time histories have been investigated and are found to exhibit large overshoots at the shock front. Although much is known about these radiation profiles, the mechanisms producing the excited states and their rate constants are unknown. To understand fully the luminous front in shock-heated air and to be able to extrapolate to experimentally-uninvestigated conditions, it is imperative that these mechanisms and their rates be known.
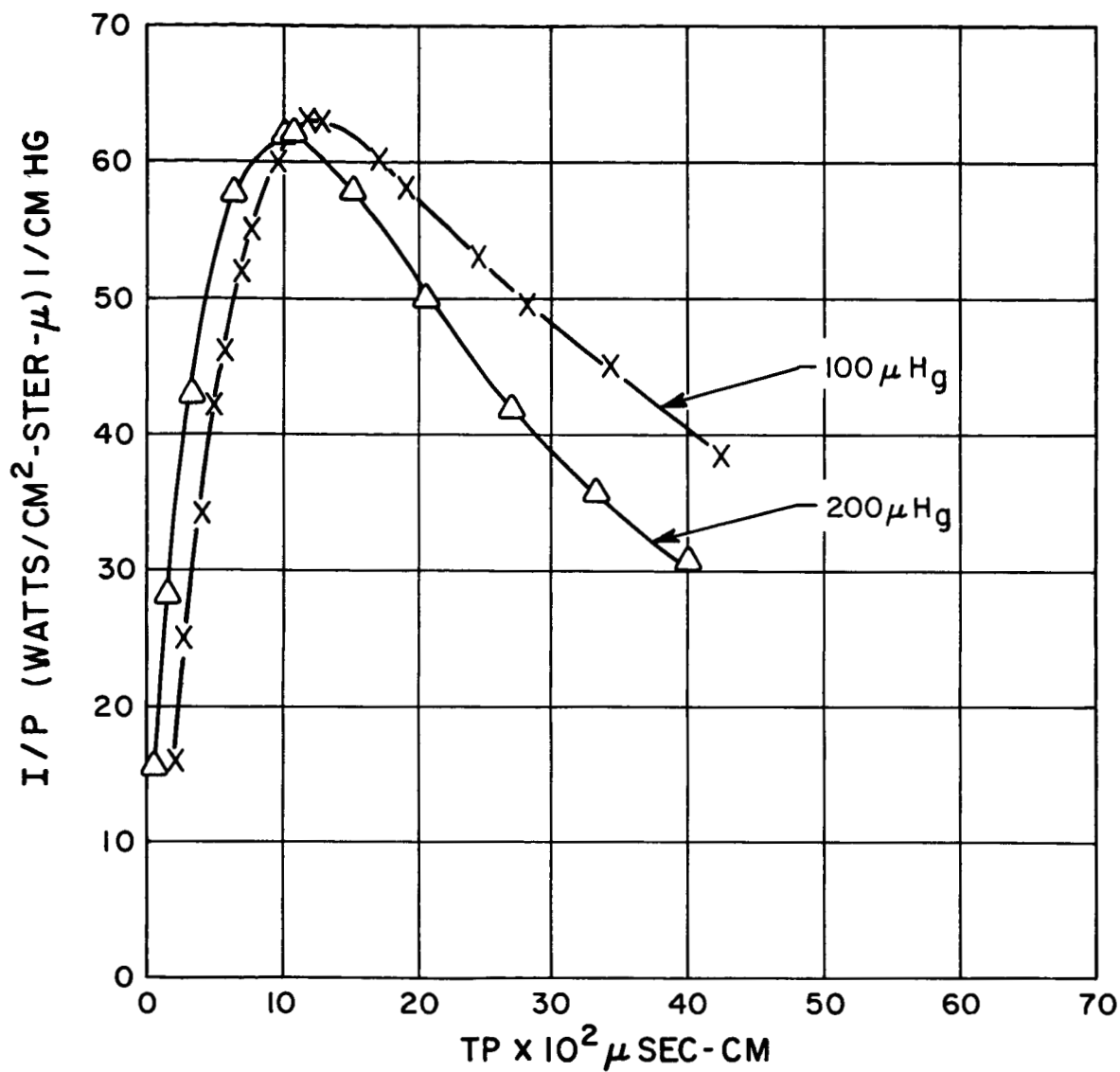
Fig. 2 Radiation intensity profiles of N_2^+ first negative system showing binary scaling. In plotting these profiles the intensity, I, for a 30 cm path length has been divided by the initial pressure, P, in cm Hg; and the time, T, has been multiplied by P. The shock velocities for the two runs were $5.22 \pm .01$ mm/μ sec.

8496

Fig. 3 N_2^+ first negative radiation profiles for 100μ and 20μ Hg initial pressure showing a breakdown in binary scaling. These profiles have been plotted as in Fig. 2. The shock velocities for these runs were 5.77 ± .02 mm/μ sec.

Thorson and Childs[8] have proposed that nitrogen in the $B^3\pi$ state is formed in the following manner:

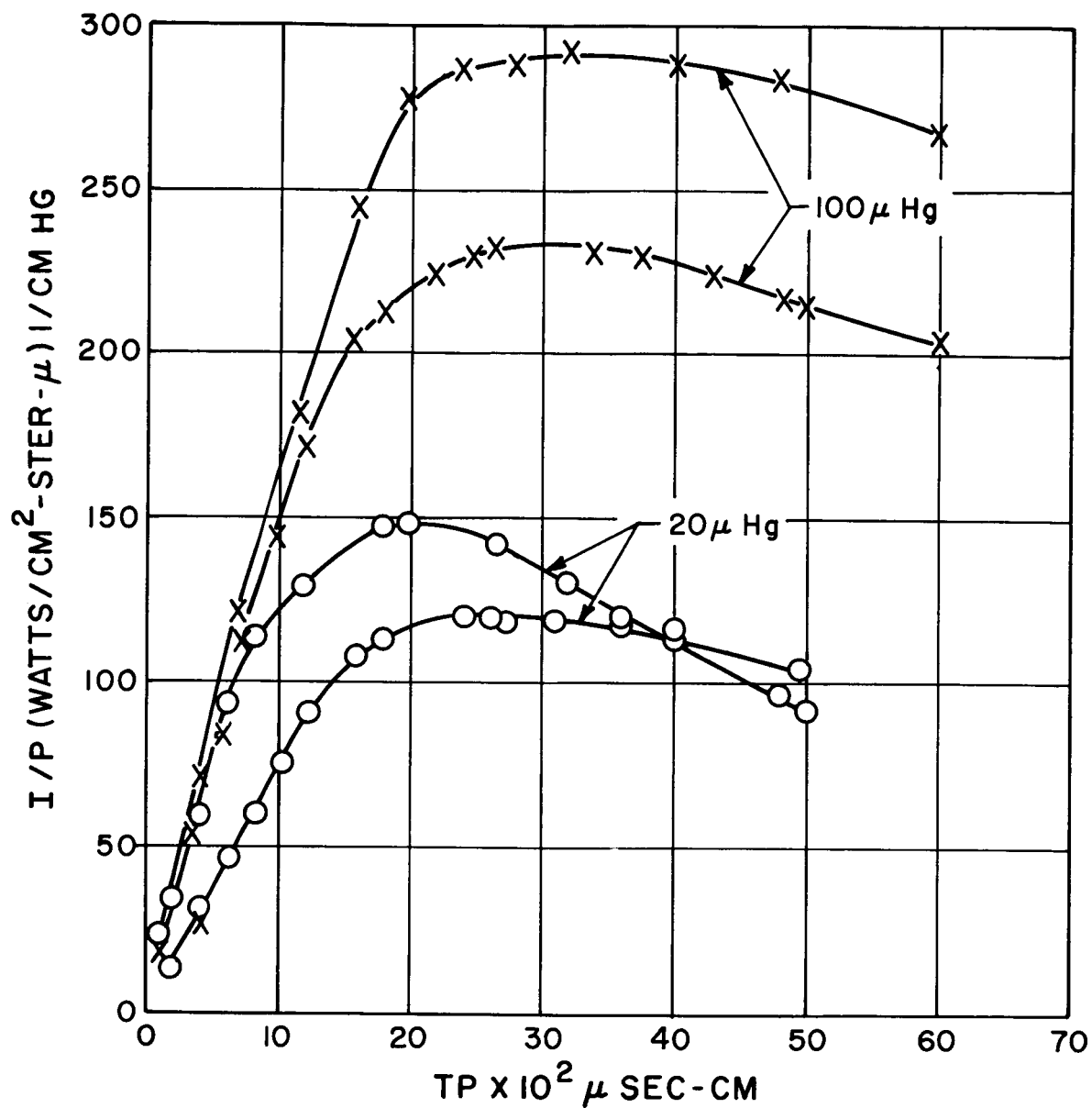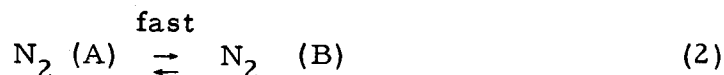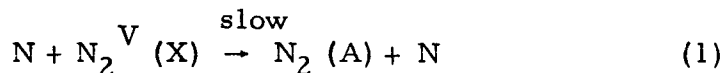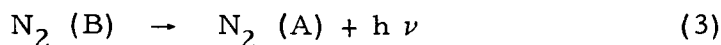$$N + N_2^{V} (X) \xrightarrow{slow} N_2 (A) + N \tag{1}$$

$$N_2 (A) \xrightleftharpoons{fast} N_2 (B) \tag{2}$$

giving rise to the N_2 (1+) radiation by the transition

$$N_2 (B) \rightarrow N_2 (A) + h\nu \tag{3}$$

That is, that the rate limiting step in the excitation mechanism is governed by reaction (1) and that the higher electronic states are in equilibrium with the $(A^3\Sigma)$ state. Note that the proposed rate limiting step utilizes an N-atom to excite the vibrationally excited N_2 $(X^1\Sigma)$ molecule to the (A) electronic state and that direct excitation by molecule-molecule collisions is unimportant. Hence, in a nitrogen shock, excitation must wait for production of N-atoms.

The N_2^+ (1-) radiation must await the formation of the N_2^+ ion molecule which is probably formed via the reaction

$$N + N \rightarrow N_2^+ + e \tag{4}$$

If the above mechanisms be true, the luminous front in a shock-heated N-N_2 mixture should be significantly changed from that of pure N_2 and the rate of reaction (1) and perhaps (4) can be measured by the rise of radiation. Some preliminary calculations have been made and an experiment to test this hypothesis has been designed. Most of the apparatus has been assembled and some preliminary experiments have been carried out.

Preliminary calculations indicated that a sufficient N-atom concentration could be maintained in a 10 ft. long, 1-1/2 in. diameter glass test section in which the atoms are produced by means of a pulsed electric discharge between electrodes located at opposite ends of the test section. For initial N_2 pressures of the order of 1 mm, the atoms will last for times of the order of one second before their disappearance due to three-body recombination in the gas phase and wall recombination. Diffusion of the atoms along the tube to the electrodes is unimportant. The gas cools to room temperature in times of the order of 10 m-sec.

A conventional chemically-driven shock tube has been set up using a test section as described above. Preliminary measurements of atom concentrations have been made by monitoring the characteristic yellow afterglow

with a photomultiplier filter combination which is peaked at 5900A. Using the known value for the three-body recombination rate of nitrogen[9] in conjunction with the afterglow intensity decay, we have found that atom concentration up to 50% have been produced. Typically, 80 m-sec following the discharge (initial N_2 pressure = 1 mm) atom concentrations are of the order of 10 to 20%.

We have run a few shock waves into such N-N_2 mixtures and have monitored the N_2 (1+) with a photomultiplier filter combination which is peaked at 6250A and the N_2^+ (1-) with a photomultiplier filter combination which is peaked at 4250A. The experiment at the present time looks promising as some difference between the N-N_2 and pure N_2 luminous fronts has been detected. It is to be emphasized that these are very preliminary results and that in the near future our final optical monitoring systems will be completed and final judgement on the value of the experiment must be reserved until then.

4. Shock Front Radiation - Theory *

Calculations have been performed to determine the shock front radiation history for local equilibrium for the N_2 (1+) bands. For the non-equilibrium radiation of the N_2 (1+) band system, the upper electronic state was assumed to be in thermal equilibrium with the ground state at the vibrational temperature. Runs were made for the following shock speeds and pressures: U_S = 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10 mm/μ sec; p = 1.0, 0.3, 0.1, 0.03, 0.01, and 0.003 cm of mercury. These cases gave us 42 conditions to evaluate, covering the extremes of shock speed and pressure which are normally run in this laboratory. (Some runs at even lower pressures have been made here recently.)

The following parameters were calculated: time for the peak of radiation, time for equilibrium radiation, time for the back reaction to set in (i.e., the recombination of atoms is 10% of the dissociation), and the peak to equilibrium ratio of radiation.

The time of the peak of radiation always corresponded to the point where the vibrational temperature became equilibrated with the translational temperature. This was to be expected because the radiation was held in equilibrium with the vibrational temperature. However, the experimental runs did not show a peak of radiation at our vibrational peak time. There are two explanations for this: (1) the vibrational temperatures are not calculated correctly, and/or (2) the upper electronic states are not excited at the vibrational temperature. There is good reason to be suspicious of our C. V. D.

scheme which calculates the vibrational temperature history. Our present C.V.D. scheme does not take into account the depletion of upper states due to dissociation, and uses a harmonic oscillator well which requires the ladder climbing process to occur one step at a time. Efforts are being made to correct these deficiencies. In addition, there is no good reason to require the upper electronic states to be excited at the vibrational temperature unless only molecule-molecule collisions take place. If atoms excite the molecules then the translational temperature will play an important role.

When the back reaction sets in, the process is no longer a two-body process, but a three-body process; i.e., $N_2 + A \rightleftharpoons N + N + A$, where A is some catalyst. This means that the reactions cannot be binary scaled as in a two-body process so that certain parameters will not be sufficient to describe the radiation profile under all conditions. At the lower shock speeds (i.e., below 7 mm/μ sec) and lower pressures (below .1 cm) the back reaction sets in after the peak. There were some calculations in which a peak did not occur at all, a condition not seen in the experimental runs at this laboratory.

The peak to equilibrium ratios calculated were uniformly higher than those obtained by the experiments except for those calculations made at very high shock speeds and pressures where no peak occurred at all.

Alternative methods of excitation are being examined which may help clear up some of the discrepancies between this theoretical model and experiments. For example, as discussed in the previous section, it is possible that atoms play a very important role. This means that the translational temperature will play an important role. The translational temperature is peaked initially, so that the only possible result is to shift the peak of radiation to earlier times more in agreement with experiment. In ordinarily shocked gas, there are no atoms present so that the radiation does not build up so rapidly. This will surely bring down the peak if an atom exciting mechanism is used. In addition, finite cross sections will introduce a time delay and slow down the speed of the reaction. A local equilibrium theory naturally assumes infinite cross-sections. If the experiment of shocking a partially dissociated gas is successful, it will be possible to obtain the cross-sections for atom-molecule processes by direct experiment. It is hoped that some of these refinements can be performed in the future after the experiments previously discussed have progressed further.

Other related work has been a new calculation of overlap integrals. Using our scheme, we can calculate all overlap integrals in a band system from the (0, 0) transition. This was made possible from a rigorous derivation of recursion formulas of the various wave functions for a Morse oscillator which is used to calculate these wave functions. The (0, 0) transition presents an extremely difficult integral and has been solved so far by the method of steepest descents. For the four band systems tried, the results have been excellent, agreeing almost exactly with previously quoted results.

In the near future, overlaps will be calculated for the following band systems which occur in shock tube work: N_2 (1+), N_2 (2+), N_2^+ (1-), N_2^+ (Meinel), NO (β), NO (γ), NO (Ogawa), O_2 (S.R.), CN (Red), CN (Violet),

CO^+ (Comet tail), C_2 (Swann) and NH. These calculations should run off very quickly and will be published.

5. Current Assessment

Sufficient coverage of non-equilibrium radiation has been made to make a reasonably good estimate of the significance of this source of heating for the Apollo re-entry problem. The measurements made in our shock tubes appear to be in good agreement with available ballistic range results. Sufficient density coverage has been achieved to validate binary scaling and preliminary experiments at low densities in nitrogen have detected collision limiting. From these experimental studies, our gross understanding of the non-equilibrium radiation is felt to be sufficient to enable us to scale the available measurements over the flight spectrum of interest to an Apollo Re-entry Vehicle.

The details of excitation of this radiation in an air shock and exactly how to rigorously include this effect theoretically into flow calculations still remains unknown. However, related experiments and theoretical studies in constituent gases are presently in progress to advance our understanding of this aspect of the problem.

6. Planning Next Three Months

A. Experimental

1. Continue monochromator measurements in wavelength region beyond 1.0μ. These measurements have been in progress for the past few weeks and the data is now in the process of being analyzed.

2. Make more accurate measurement of Kramer's radiation. This will be accomplished in conjunction with the monochromator measurements beyond 1.0μ.

3. Continue with atomic-molecular electronic excitation mechanism experiment, (shocks in $N-N_2$ mixtures).

B. Theoretical

1. Incorporate present experimental knowledge of non-equilibrium radiation into flow calculations.

2. Revise equilibrium radiation estimates in line with an up-to-date knowledge of f numbers Kramer's radiation, and atomic line radiation.

REFERENCES

1. Avco-Everett Research Laboratory Final Phase I Report, "Study of Thermal Radiation Associated with Non-Equilibrium Flow in the Apollo Flight Regime," Contract No. NAS 9-156, March 1962. (CONFIDENTIAL)

2. Keck, J. C., Camm, J. C., Kivel, B., and Wentink, T. Jr., "Radiation from Hot Air," Annals of Physics, 1 May 1959; also, Avco-Everett Research Laboratory Research Report 42.

3. Allen, R. A., Camm, J. C. and Keck, J. C., "Radiation from Hot Nitrogen," Avco-Everett Research Laboratory, Research Report 102. April, 1961. Also, J. Q. S. R. T., March 1962.

4. Kivel, B. and Bailey, K., "Tables of Radiation from High Temperature Air," Avco-Everett Research Laboratory Research Report 21, December 1957.

5. Lindenmeier, C. W., "Kramers' Radiation from Hot Air," Avco-Everett Research Laboratory Research Note 157, September 1959.

6. Teare, J. D., Georgiev, S., and Allen, R. A., "Radiation from the Non-Equilibrium Shock Front," Avco-Everett Research Laboratory Research Report 112, October 1961.

7. Allen, R. A., Keck, J. C., and Camm, J. C., "Non-Equilibrium Radiation from Shock Heated Nitrogen and a Determination of the Recombination Rate," Avco-Everett Research Laboratory, Research Report 110, June 1961. Physics of Fluids, March 1962.

8. Avco-Everett Research Laboratory Re-entry Physics Program Monthly Report, Contract DA-19-020-ORD-5476, October 1961.

9. Wentink, T. Jr., Sullivan, D. O., and Wray, K. L., "Nitrogen Atomic Recombination at Room Temperature," Avco-Everett Research Laboratory, AMP 18, May 1958.

THIS PAGE IS BLANK